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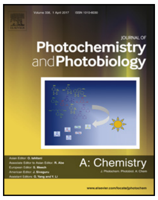

Effect of *p*-nitrophenol degradation in aqueous dispersions of different crystallized goethites

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ABSTRACT

Different crystallized goethites (α-FeOOH) were obtained via air oxidation. The reductive transformation and oxidative degradation of *p*-nitrophenol (PNP) was evaluated with as-prepared α-FeOOH as catalyst. Results showed that the α-FeOOH sample exhibited high reactivity for reduction transformation and oxidative degradation of PNP with decreasing degree of catalyst crystallization. In α-FeOOH/Fe(II) systems, low-crystalline α-FeOOH showed high surface-bound Fe(II) contents on the catalyst surface, which led to elevated PNP rates of reduction transformation. *p*-Aminophenol (PAP), as the main reduction transformation product of PNP, could be removed and mineralized further by photo-Fenton reaction in the low-crystalline α-FeOOH/H_2O_2 system under visible light irradiation. A possible mechanism was suggested for the comprehensive effect of PNP degradation during the reaction process.

1. Introduction

p-Nitrophenol (PNP), one of the most commonly used nitroaromatic compounds, is often found as a pollutant in chemical industrial wastewater [1]. Given its toxicity and hazard, PNP is regarded as one of the priority pollutants by the US Environmental Protection Agency (EPA) [2]. Current technologies for the removal of PNP include membrane filtration, photodegradation[3], adsorption [4], and chemical reduction[5–8]. Nevertheless, conventional treatment approaches present several major shortcomings. The slow degradation rate, limited degradation efficiency, secondary pollution, high costs, and strict operating conditions remarkably limit their wide applications in large-scale production [9–11]. Among various treatment techniques, the chemical reduction of PNP to *p*-aminophenol (PAP) is a favorable route because the generated PAP serves as an important intermediate for cosmetic products, analgesics, and antipyretics [12]. Moreover, PAP is relatively less toxic and easier to be removed and mineralized compared with nitroaromatic compounds [13].

Iron hydroxides are important natural reductants. Among the different iron hydroxides, α-FeOOH has stable chemical properties, and it is widely used as a reductant and catalyst for environmental remediation applications [14–16]. The preparation of highly catalytic active α-FeOOH is important in environmental chemistry. Studies have reported that catalytic activity is associated with the crystallization of particles. Results demonstrate that low-crystalline particles exhibit high catalytic activity [17–19]. Our previous studies revealed that the low-crystalline α-FeOOH phase can be obtained via air oxidation in the presence of ethylenediaminetetraacetic acid (EDTA) under light irradiation [20,21]. We proposed that low-crystalline α-FeOOH should be highly active toward PNP degradation. Some reports have illustrated that mineral-bound Fe (II) species on the iron (hydr)oxide surface can substantially promote the reduction transformation of nitrogroup to the corresponding aniline under anaerobic conditions [22–24]. The electron exchange between adsorbed Fe(II) (Fe(II)ads) and structural Fe(III) of iron (hydr)oxides is important to understand the reduction transformation of nitroaromatic compounds [25–27]. However, the comprehensive effect of PNP degradation between reductive transformation of PNP and oxidative degradation of transformation product (PAP) of PNP at the same reaction system using low-crystalline α-FeOOH as catalyst has not been reported.

In this study, different crystallized α-FeOOH samples were obtained via air oxidation. PNP was selected as the representative

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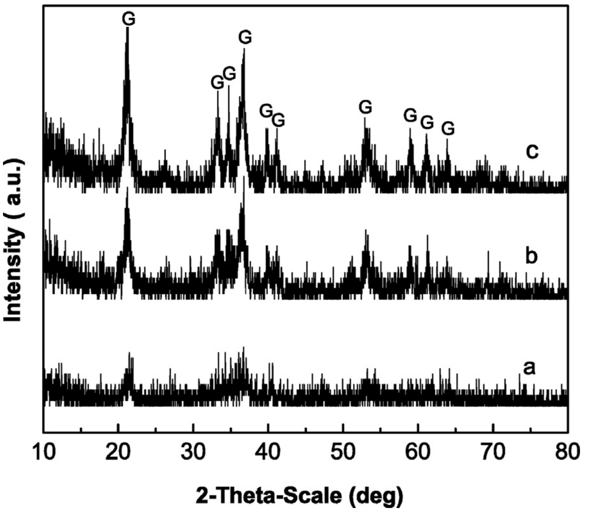

Fig. 1. XRD patterns of as-prepared samples (a: G-150-20; b: G-0-20; c: G-0-50; G: α-FeOOH).

of nitroaromatic compounds. The reductive transformations of PNP in the presence of trace Fe(II) ions and oxidative degradation of reduction transformation product (PAP) of PNP by the as-prepared α-FeOOH catalyst, were investigated. The comprehensive effect of PNP degradation during the reaction system was also determined.

2. Experimental section

2.1. Materials

Ferrous sulfate ($FeSO_4{\cdot}7H_2O$), ethylenediaminetetracetic acid (EDTA), sodium hydroxide (NaOH), Hydrochloric acid (37% HCl), hydrogen peroxide (30% H_2O_2), *tert*-butanol, *p*-benzoquinone (BZQ), disodium ethylenediaminetetraacetate (Na_2-EDTA), *p*-nitrophenol (PNP) and *p*-aminophenol (PAP) were of analytical purity and were purchased from Zhiyuan Chemical Reagen Co., Ltd. (Tianjin, China). Distilled water was used.

2.2. Preparation of different crystallized α-FeOOH samples

Low- and relatively high-crystallized α-FeOOH samples were obtained via air oxidation at 20°C at pH 8.7 in the presence of EDTA (1 mM) by controlling the visible light intensities at 0 and 150 lx, respectively, which was reported in our previous study [20]. The as-prepared samples at 20 °C under light irradiation at 0 and 150 lx were denoted as G-0-20 and G-150-20, respectively. Using the same preparation methods, high-crystallized α-FeOOH was obtained at 50°C by controlling the visible light intensities at 0 lx(a dark reaction was simulated in an iron case), which was denoted as G-0-50.

2.3. Adsorption experiments

α-FeOOH (0.3 g) was added to 100 ml of PNP solution with varying concentrations at pH 9.0 in polyethylene centrifuge tubes. The mixture was agitated for 10 h in a thermostatic shaker bath under N_2 at 20 °C. Samples were centrifuged to separate the solid catalyst from aqueous solution. The supernatants were then analyzed using a UV–vis spectrometer at 400 nm, and the adsorption capacity was calculated using the Langmuir adsorption model equations [28,29].

2.4. Reductive transformation experiments of PNP

Reductive transformation experiments of PNP were performed in degassed PNP solutions (2.5 mM, 100 ml). A fixed amount of α-FeOOH (0.3 g) was added to the PNP solutions. Fe^{2+} ions (1.5 mM $FeSO_4$) were dripped simultaneously into the reactor via a peristaltic pump under stirring. The mixtures were adjusted to pH 9.0 by adding 1.0 m NaOH. Reactions were conducted in a dark iron case at room temperature (20°C). N_2 flow was bubbled throughout the reaction system to remove dissolved oxygen. At the selected time interval, the suspensions were centrifuged for 5 min. The concentrations of PNP were determined using a UV–vis spectrometer at 400 nm. The reduction transformation efficiency (RTE) of PNP was calculated from the following equation:

$$\mathrm{RTE}(\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

where C_0 and C are the concentration of PNP at time 0 and t, respectively.

2.5. Oxidative degradation of reductive transformation product (PAP) of PNP

The main product of PNP reduction transformation was PAP. Oxidative degradation experiments of the generated PAP were continued in the above reaction system. The air (flow rate = 0.272 $m^{3}\bullet H^{-1}$), which replaced N_2 flow, was passed through the suspension at 20°C. Subsequently, H_2O_2 (2 mM) was added to the reaction system at the beginning of irradiation by a 100 W incandescent lamp.

By contrast, we simulated the above PAP system with the same concentrations of H_2O_2, Fe^{2+} ions and PAP (using purchased PAP as pollutant). Then the same amount of as-prepared α-FeOOH catalyst was added into the PAP-simulated reaction solution. And the pH remained the same in both systems. The oxidative degradation experiment of the purchased PAP was performed under similar reaction conditions.

At the selected time interval, the suspensions were centrifuged for 5 min. The concentrations of PAP in the reaction system were measured by a UV–vis spectrometer at 631 nm. The concentrations of Fe(II) and total iron ions in solution were determined by the 1,10-phenanthroline method [30].

2.6. Sample characterizations

X—ray diffraction (XRD) patterns were obtained on a Bruker diffractometer using a Cu Kα radiation. The crystallinity of samples were determined from the peak area between 2θ= 21.2 and 36.7° using a highly crystalline α-FeOOH sample (supplied by Tianjin Chemical Reagents Company) as a reference. Characterization FT-IR spectra were recorded in the region of 500–4000 cm^{-1} using a Bruker Tensor 27 Infrared spectrometer. TEM images were obtained with a Hitachi H-7500 transmission electron microscope. The BET surface areas were measured by multipoint N_2-BET analysis using a Quantachrome (NOVAe) surface area analyzer. The content of surface-bound Fe(II) species was calculated by Li. et al. reported method [31]. ^{1}H NMR spectra were recorded on a AV III-300 BRUKER spectrometer. The electrospray ionization mass spectrometry (ESI) were obtained with a AB SCIEX 3200Q-TRAP mass analyzer at a typical ESI conditions. UV–vis diffuse reflectance spectra (UVDRS) were obtained using a UV–vis spectrometer (U-3010, Hitachi) equipped with an integrating sphere assembly. Total organic carbon (TOC) was analyzed with a lquiTOC II analyzer (Elementar Analytik, Germany).